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The ferromanganese production using Indonesian low-grade manganese ore using charcoal and palm kernel shell as reductant in mini electric arc furnace

Y I Supriyatna[1], Z Zulhan[2], and Y Triapriani

[1]Research Unit for Mineral Technology, Indonesian Institute of Sciences, Lampung 35361, Indonesia.
[2]Department of Metallurgical Engineering, Bandung Institute of Technology, Bandung 40132, Indonesia

Email: yayat_iman@yahoo.com

Abstract. The series of ferromanganese production have been conducted using charcoal and palm kernel shell as a reducing agent to replace of cokes. The experiment was preceded by the characterization of raw materials. Manganese ore and limestone were analyzed using XRF and XRD. Charcoal and palm kernel shells were analyzed proximate to determine its carbon content. Based on the analysis of raw materials then calculated mass balance to determine the raw material requirements for each experiment. The variations are the use of reductant ratio (1, 1.5 and 2.1 stoichiometric ratio). Products and slag are analyzed using OES and AAS to determine its chemical composition. The results showed that the use of palm kernel shell as a reductant better than charcoal for all use ratio (1, 1.5 or 2.1 stoichiometric ratio). The highest percentage of manganese extraction using palm kernel shells as a reducing agent is 49.91% (75.58% Mn, 15.75% Fe, 2.12% C, 5.23% Si, 0.08% P) with the product of FeMn is 6,6 kg. The highest percentage of manganese extraction using charcoal as reductant is 44.16% (72.35% Mn, 18.44% Fe, 1.93% C, 5.69% Si, 0.02% P) with the product of FeMn is 6,1 kg. The results showed that palm kernel shell and charcoal could potentially be used as a reductant in the production ferromanganese.

1. Introduction

Indonesia has the potential of manganese reserves contained in several locations such as Sumatra, Java, Nusa Tenggara Timur and a small portion in Kalimantan, Sulawesi, and Papua. Reserve of manganese in Java Island based on data from Center for Geological Resources (PSDG) – The Ministry of Energy and Mineral Resources (ESDM) is in West Java (Sukabumi, Tasikmalaya), Central Java (Kebumen, Magelang and Wonogiri) and East Java (Blitar, Jember, Malang, Pacitan, Trenggalek, Tulungagung)[1]. Manganese resources of which there are fairly large in East Java province. Complete data about the mineral resources of manganese in East Java province is shown in Table 1.

Until the end of 2013, more manganese is exported in raw material form without unprocessed. On January 12, 2014, Act No. 4 of 2009, on the obligation for the holder of Mining Business License (IUP) and Special Mining Business License (IUPK) to increase value-added products of mineral and coal through processing and refining, formal applicable. In Article 103 paragraph 1 states that "Holders of Production Operation IUP and IUPK are required to perform processing and refining of mining production in the country" [2]. Associated with added value activities of minerals through processing and refining are regulated and clarified through the regulation No 7 of 2012 Minister of Energy and Mineral Resources. The regulation amended several times. Recent changes are regulation of ESDM RI No 8 of 2015 concerning mineral added value through Activities of Mineral Processing and Purification whose set a minimum limit for the product of processing and/or purification for 12 metallic minerals. Manganese minerals in accordance with Annex I ESDM No. 8 of 2015 abaout minimum limit of processing and refining within the country in form ferroalloys is ferromanganese with Mn contents □ 60% [3].

A ferromanganese is an alloy form between the iron and manganese elements in which manganese is the dominant element. The content of manganese in ferromanganese generally ranges between 70% - 90% Mn. The content of the other elements in these alloys, among others, carbon (C) up to 7.5%, Si up to 3%, P up to 0.4% and S up to 0.05%, the rest consisting of elemental iron (Fe) [4].

Another type of iron and manganese alloy with manganese contents lower (10-25%) is known as Spiegel Eisen. Classification this ferromanganese showed in Table 2.

Table 1. Manganese mineral resources in East Java Province [1]

No	District / Town	Locations	Sub-district	Resource (ton)	Information
1.	Tulungagung	Trenggalek	Basuki, Watulimo	214	Hypothetical
		Sukerejo	Rejotangen	530	Hypothetical
		G. Cemenung	Rejotangen	54,000	Mn content : 47,9% (measured)
2.	Blitar	Daerah Tambakrejo, Wlingi	Tambakrejo, Wlingi	2,000	Measured
		G. Jimbe, G. Puncukasem, Wlingi	Wlingi	22,000	Mn content : 34,24% - 41,43% (measured)
3.	Jember	Karangbale, G. Marcondon, Sekunir	Puger	489,563	Designated
4.	Pacitan	Tegalombo dan Bandar	Tegalombo, Bandar	18,315	Measured
5.	Trenggalek	Daerah Kec. Bandung	Bandung	45,000	Measured
		Desa Melis dan Sukorame	Gandusari	3,000,000	MnO_2 content : 79,4% (reserve)
6.	Lumajang	Ds. Kalirejo	Donomulyo	30,000	Mn content : 50-90% (Designated)

Table 2. Classification of ferromanganese according to ASTM standards [5]

Elements (%)	Low Carbon Ferromanganese		Medium Carbon Ferromanganese				High Carbon Ferromanganese (standard)		
	Grade A	Grade B	Grade A	Grade B	Grade C	Grade D	Grade A	Grade B	Grade C
Mn	85-90	80-85	80-85	80-85	80-85	80-85	78-82	76-78	74-76
C (max)	0.75	0.75	1.50	1.50	1.50	1.50	7.50	7.50	7.50
Si (max)	2.00	5 – 7	1.50	1.00	0.70	0.53	1.20	1.20	1.20
P (max)	0.20	0.30	0.30	0.30	0.30	0.30	0.35	0.35	0.35
S (max)	0.02	0.02	0.02	0.02	0.02	0.02	0.05	0.05	0.05

Raw materials for both methods were manganese ore. Reducing agents are cokes or coal and as a flux used limestone. The reduction reaction that occurs in the element of Mn and Fe in the ferromanganese smelting process is [6]:

$$MnO_{2\,(s)} + ½\, CO_{(g)} = ½\, Mn_2O_{3(s)} + ½\, CO_{2(g)} \qquad \Delta H_{298} = -99{,}4\ kJ \qquad (1)$$

$$Mn_2O_{3(s)} + 1/3\, CO_{(g)} = 2/3\, Mn_3O_{4(s)} + 1/3\, CO_{2(g)} \qquad \Delta H_{298} = -66{,}5\ kJ \qquad (2)$$

$$Mn_3O_{4(s)} + CO_{(g)} = 3\ MnO_{(s)} + CO_{2(g)} \qquad \Delta H_{298} = -51{,}2\ kJ \quad (3)$$

$$1/3\ C_{(s)} + 1/3\ CO_{2(g)} = 2/3\ CO_{(g)} \qquad \Delta H_{298} = +57{,}5\ kJ \quad (4)$$

$$½\ Fe_2O_{3(s)} + 3/2\ CO_{(g)} = Fe_{(s)} + 3/2\ CO_{2(g)} \qquad \Delta H_{298} = -11{,}59\ kJ \quad (5)$$

$$½\ Fe_2O_{3(s)} + 3/2\ C_{(s)} = Fe_{(s)} + 3/2\ CO_{(g)} \qquad \Delta H_{298} = +247{,}1\ kJ \quad (6)$$

$$MnO_{(l)} + C_{(s)} = Mn_{(l)} + CO_{(g)} \qquad \Delta H_{298} = +236{,}4\ kJ \quad (7)$$

$$SiO_{2\,(l)} + 2C_{(s)} = Si_{(l)} + 2\ CO_{(g)} \qquad \Delta H_{298} = +725{,}9\ kJ \quad (8)$$

Pyrolusite is the general manganese compounds contained in manganese ore, are relatively unstable and easily reduced in solid form in the presence of CO gas or under reductive conditions [7]. Currently, the main technology in pyrolusite reduction process uses coal and/or coke as a reductant and fuel. However, this reductant causes in pollution and greenhouse gas emissions. The use of fossil fuels such as coke and coal led to an increase in greenhouse gases in the atmosphere from 280 ppm to 390 ppm, which has serious impact on global warming [8].

In addition to environmental concerns, the price of coal and coke which are relatively high is another obstacle that must be faced by businessmen in order to increase production and reduce the cost of production. Therefore, manganese producers are under pressure large enough to change the existing processes and/or develop a new process that is more environmentally friendly to meet the challenge of climate change while remaining economical.

Recently, the use of biomass as a fuel and reductant in the reduction process of manganese ore has attracted a lot of attention. For example, research by Tian et al [7] in 2010 using corn cobs as a reducing agent to extract manganese from low-grade manganese ore. Research conducted Zhao et al [8] in 2010 showed manganese oxide ore can be reduced by roasting using a straw at a temperature below 650 ° C. Straw is a renewable biomass resource and can generally be found as waste in the food and agriculture industry.

Another biomass that can be used as a carbon source is palm kernel shell which is a waste of the palm oil industry. Indonesia is one of the largest producers of palm oil is about 16-17 million tons/year. Approximately 20-25% (3.5-4 million tons / year) palm kernel shells obtained from palm oil production [9]. Palm kernel shells can be converted into palm kernel shell coal that can serve as a reductant such as coal and coke. Besides palm kernel shells, carbon sources derived from biomass that can be used as a reducing agent is charcoal.

Based on these facts, these researchs was conducted to ferromanganese production using manganese ore obtained from the sub-district Puger Jember - East Java. The smelting process carried out in a mini electric arc furnace with palm kernel shells (PKS) and charcoal as a reductant. The processing time, the ratio of reductant addition and the ratio of the addition of limestone as a flux using the research results with coke as a reductant [10]. This study was a preliminary research in assessing the potential of palm kernel shells and charcoal as a reducing agent in the smelting of Indonesia manganese ore in a mini electric arc furnace.

2. Experimental Procedures

The research includes several stages as follows :

1. Preparation and analysis of manganese ore, limestone, palm kernel shells (PKS), and charcoal as a raw material for the ferromanganese production. Cokes and charcoal are crushing to obtained a similar size that is 2-4 cm. Manganese ore and limestone were crushing to obtained a size of 1-3 cm. Then, manganese ore and limestone were grinding using ball mill up to -200 mesh for analyzed using XRF and XRD to determine contents of elements and compounds present in the raw material. Palm kernel shells and charcoal was proximate analyzed to determine the carbon content.
2. Subsequent experiments are ferromanganese production using PKS and charcoal as a reductant in mini electric arc furnace (Figure 1). The experiment process of smelting manganese ore in an electric arc furnace begins by dividing the raw material equally into 6 parts according to its composition. The first and second enters for the beginning of the

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process. Then the three, four, five and six sections are entered at an interval of 5 minutes. Temperature measurements using immersion thermocouple (NSP 203R C / AL model) were performed prior to the pouring process of metal and slag. The melted metal and slag are poured into the mold that has been provided.

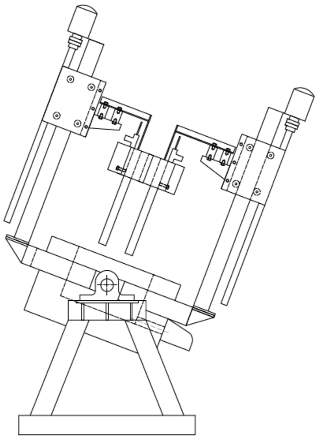

Figure 1. Design of mini Electric Arc Furnace

3. Analysis of the product and the slag from an experiment using OES and AAS to obtain the effect of variations reductant into the percentage of manganese extraction.

3. Results and Discussion

3.1. Characteristics of Raw Materials

The chemical composition of raw materials can be seen in Table 3 to Table 5.

Table 3. Chemical composition of Limestone

Compound	Amount (%)
CaO	55.65
SiO_2	0.13
Al_2O_3	0.22
Fe_2O_3	0.20
MgO	0.01
MnO	0.63
Na_2O	0.01
K_2O	0.04
TiO_2	0.03
P_2O_5	0.02
SO_3	0.00
LOI	43.06

Table 4. Chemical composition of Manganese Ore

Compound	Amount (%)
MnO_2	52.7
SiO_2	29.11
Al_2O_3	2.46
Fe_2O_3	8.17
TiO_2	0.12
K_2O	1.06
CaO	2.67

MgO	0.57
Cr_2O_3	1.36
P_2O_5	0.16
CuO	0.071
BaO	0.59
SO_3	0.003
Co_2O_3	0.001
NiO	0.002
PbO	0.59
ZnO	0.24
SrO	0.084
Y_2O_3	0.001

Table 5. Result of Proximate Analysis

Compound	Palm Kernel Shell	Charcoal
Fixed Carbon (wt%)	21.11	76.85
Volatile Matter (wt%)	67.43	8.75
Ash (wt%)	2.30	4.37
Moisture (wt%)	9.16	10.03

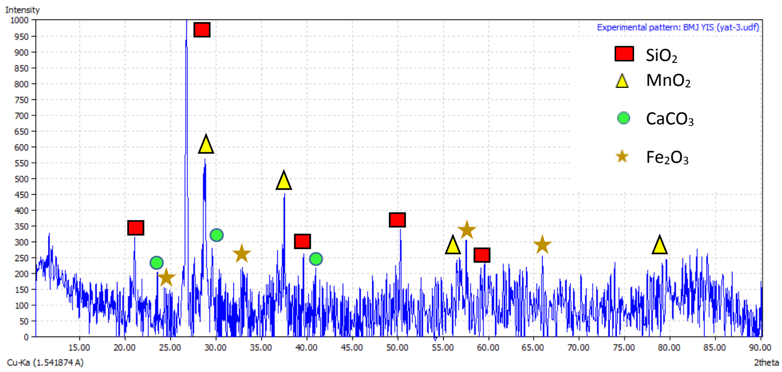

Figure 2. XRD pattern of manganese ore

The results of XRF analysis (Table 1) and XRD (Figure 2) show that the most dominant compound in the manganese ore is Pyrolusite (MnO_2). Other detected compounds are SiO_2, Fe_2O_3, and $CaCO_3$.

3.2. Result of Smelting Process

In these experiments, the processing time and the addition of limestone, using data from previous studies conducted Yayat et al [10]. The addition of limestone is 7 kg and processing time is 70 minutes. Manganese ore is used 30 kg.

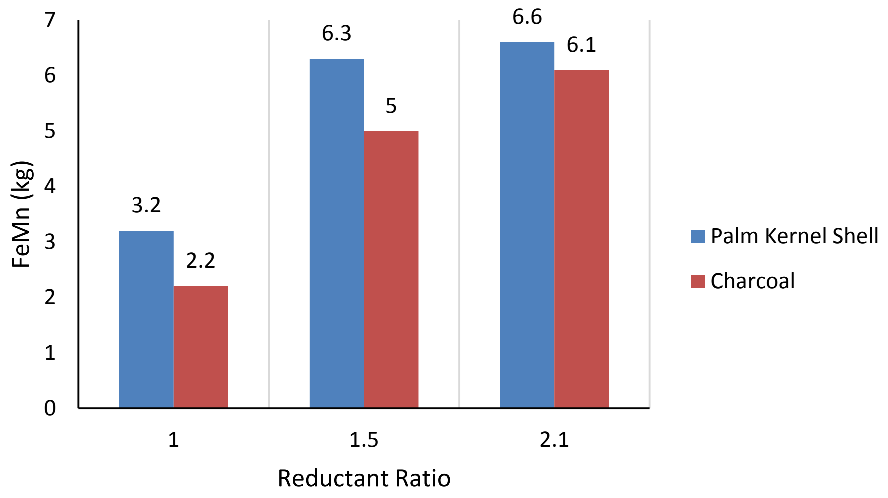

Figure 3. Effect of reductant type to the ferromanganese product in the composition of the 30 kg of manganese ore, 7 kg of limestone and 70 minutes of the processing time

Ferromanganese products using palm kernel shells and charcoal as reductant indicate the same trend. The trend is in line with the increasing used of reductant then the ferromanganese product increased (Figure 3). This could be due to the presence of excess carbon which would keep the carbon in the system so that it can produce CO gas is needed to reduce MnO_2 to be MnO and ensuring the availability of carbon to reduce MnO in slag to metallic Mn. Based on Figure 3, when added a reductant 1 stoichiometry, 1.5 stoichiometry and 2.1 stoichiometry experimental results show the highest ferromanganese products generated using palm kernel shells as a reductant (3.2 kg FeMn for 1 stoichiometry, 6.3 kg FeMn for 1.5 stoichiometry and 6.6 kg FeMn for 2.1 stoichiometry).

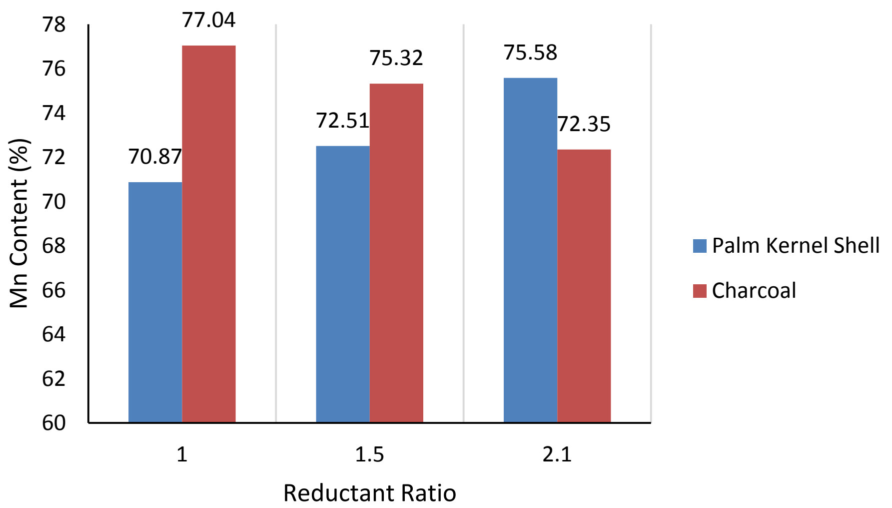

Figure 4. The influence of reductant type on Mn content in the product on the composition of 30 kg of manganese ore, 7 kg of limestone and 70 minutes of the processing time

The manganese content results of the experiment showed different trends for different types of reductant. Palm kernel shells indicate increased usage of reductant then the manganese content is also increasing. The increasing use of charcoal reductant then the manganese content in the product obtained a slight decline (Figure 4).

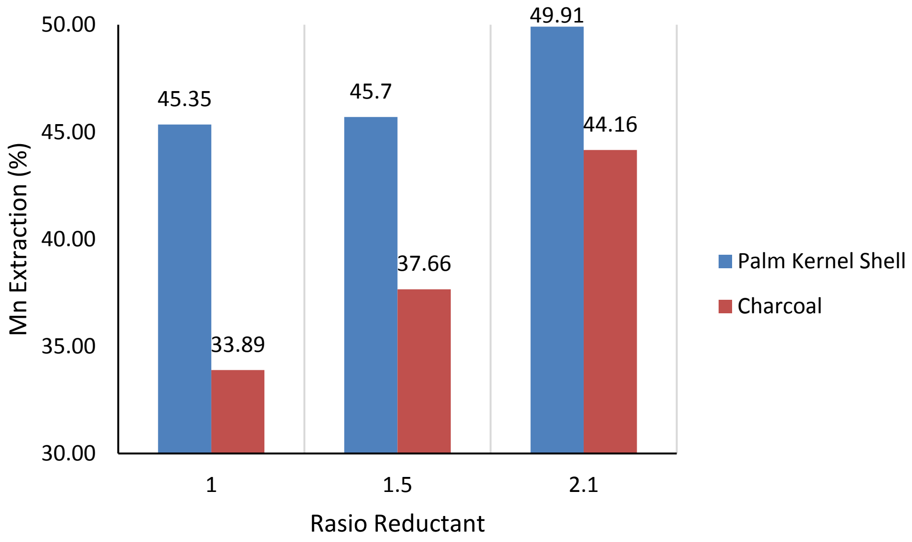

Figure 5. The influence of reductant type on Mn extraction percentage on the composition of 30 kg of manganese ore, 7 kg of limestone and 70 minutes of the processing time.

The highest percentage of manganese extraction for 1 stoichiometry, 1.5 stoichiometry and 2.1 stoichiometry obtained using palm kernel shells as reductant (Figure 5). The highest percentage of manganese extraction for reductant palm kernel shells or charcoal obtained in 2.1 stoichiometry.

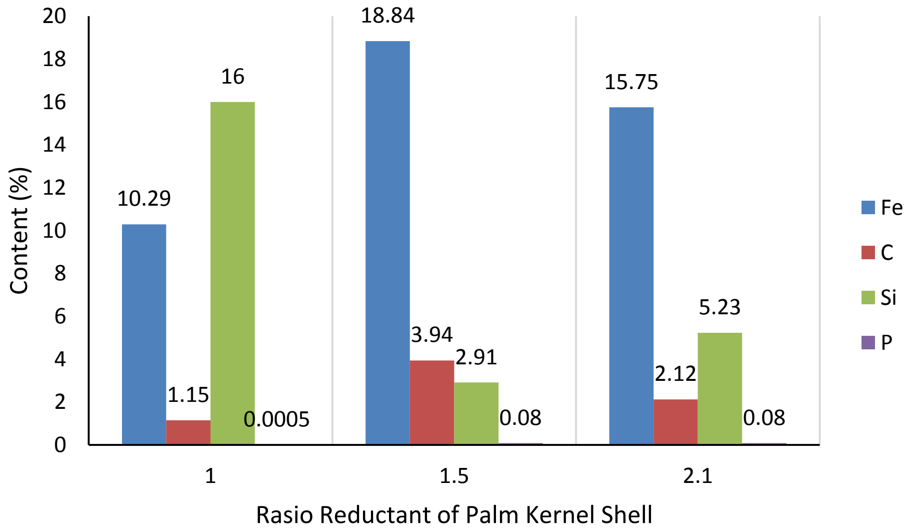

Figure 6. The effect of adding palm kernel shells as a reductant on the composition of the product composition on the 30 kg of manganese ore, 7 kg of limestone and 70 minutes of the processing time

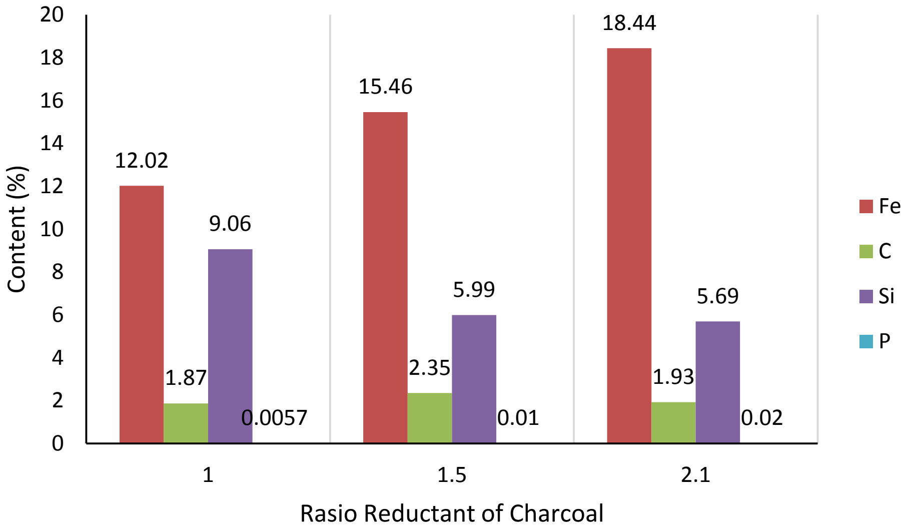

Figure 7. The effect of adding charcoal as a reductant on the composition of the product composition on the 30 kg of manganese ore, 7 kg of limestone and 70 minutes of the processing time

The results showed a trend with increasing use of a reductant (palm kernel shells and charcoal) effect to decreased of Fe content, increased of C content, increased of Si content, decreased of P content (Figure 6 and Figure 7).

4. Conclusion

The results showed that palm kernel shell and charcoal could potentially be used as a reductant in the production ferromanganese. The highest percentage of manganese extraction using palm kernel shells as a reducing agent is 49.91% (75.58% Mn, 15.75% Fe, 2.12% C, 5.23% Si, 0.08% P) with the product of FeMn is 6.6 kg. The highest percentage of manganese extraction using charcoal as a reductant is 44.16% (72.35% Mn, 18.44% Fe, 1.93% C, 5.69% Si, 0.02% P) with the product of FeMn is 6.1 kg.

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